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(56) Documents Cited

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(58) Field of Search

UK CL (Edition N ) C7B BCAX, G1B BBS, G1N NAHAS  
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## (54) Gas sensor monitoring incorporating gas generation

(57) The sensitivity, response time and the regenerative behaviour of a gas sensor 1 is monitored by producing temporary quantities of gas of the test component and supplying them to the gas sensor. The quantities of gas required for monitoring the sensor are produced electrolytically near the anode and/or at the cathode of generator cell 2 by means of reactions in which water is electrolysed so that local pH displacements occur at the anode and cathode due to production of  $H^+$  and  $OH^-$  and these ions react with compounds such as  $(NH_4)_2SO_4$  and  $KHCO_3$  in the electrolyte to produce  $NH_3$  or  $CO_2$  respectively. Fan 4 supplies the gas to the sensor. The generator cell has separated electrodes and either a gel electrolyte to restrict recombination of  $H^+$  and  $OH^-$  ions or a divider such as an ion exchange membrane between the electrodes.

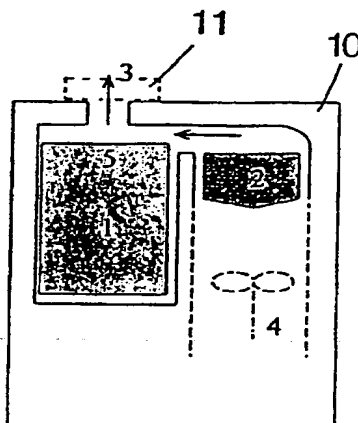


Fig.1

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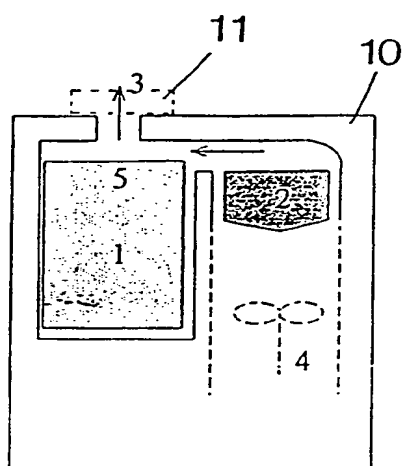
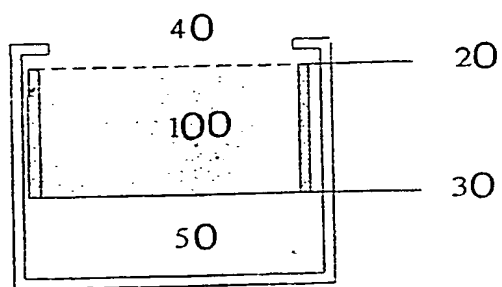


Fig. 1

2



2

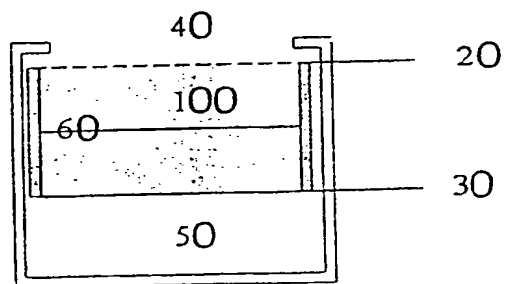


Fig. 2

METHOD AND EQUIPMENT FOR MONITORING GAS SENSORS AND ALSO  
TO THE APPLICATION OR USE THEREOF

DESCRIPTION

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The invention relates to a method and also to an item of  
equipment for monitoring gas sensors in accordance with  
the first part of claims 1 and 5. In addition to this,  
there are specified a plurality of uses in accordance  
10 with the invention of items of equipment functioning in  
accordance with the method in accordance with the  
invention.

BACKGROUND OF THE INVENTION

15

A method as well as an item of equipment of the type in  
accordance with the prior art is known from DE 26 21 677.  
There, a method as well as an item of equipment are  
described with which, or in which, temporary quantities  
20 of gas of the test component are produced and are  
supplied to the gas sensor for monitoring the sensitivity  
and/or the response time and/or the regenerative  
behaviour thereof. Thereby, the quantities of gas which  
are employed for the monitoring process are taken either  
25 from a filled reservoir or are produced by a chemical or  
direct electrochemical reaction. This method of  
generating gases is installed in static gas analysis  
systems and serves for calibrating the displayed test  
value.

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Since the prior application of use related to static gas  
analysis systems, the amount of space or the space  
requirement for such gas generators has not, up to now,  
presented any problems. If, on the other hand, one wants  
35 the gas analysis system or the gas analysing devices to  
be comprised in a smaller structure, then the gas  
generators of known type are no longer applicable.

## SUMMARY OF THE INVENTION

Consequently, the object of the invention is to develop a  
5 method or an equipment of the type in accordance with the  
prior art in such a way that the gas generators can be  
fitted into small-sized gas analysing devices and,  
moreover, that there thereby results a use in accordance  
with the invention for specific analysing devices.

10 The posed object is achieved, insofar as a method in  
accordance with the first part of claim 1 is concerned,  
by the subsequent features of claim 1. Further  
advantageous developments of the method are specified in  
15 the claims 2 to 4.

Insofar as an item of equipment in accordance with the  
first part of claim 5 is concerned, the posed object is  
achieved in accordance with the invention by the  
20 subsequent features of claim 5. Further developments are  
specified in the claims dependent on claim 5.

The many diverse ways, in which the equipment in  
accordance with the invention and which is made to  
25 function in accordance with the method in accordance with  
the invention, can be put to use, are set forth in the  
remaining claims which are set out as use claims.

It is thereby achieved, due to the invention in  
30 accordance with this method, that the process of  
generating gas can be performed in a considerably smaller  
structure. Due to this, one has been able to achieve such  
a reduction in the current consumption of these, mainly  
electrochemically functioning generators, that they can  
35 be utilised for the deployment of portable gas warning  
devices in accordance with the usages in accordance with  
the invention. The main requirement for their use in

portable gas analysis or gas warning devices is that the latter, insofar as their current supply is concerned and in contrast to static devices, have to be able to be fed merely by means of an accumulator or a battery. By virtue of the present invention, it is possible to miniaturise the gas generators in such a way that they are of approximately the same size as the miniaturised gas sensors, which are usually in the form of gel sensors, used in transportable gas warning devices. By virtue of this property, that the generators now have a very small construction, it is not only possible to employ them in portable gas warning devices because of their constructional dimensions and their very low current consumption, but also, over and above this, there is the advantage that these gas warning devices are not only capable of analysing or detecting a single component of the gas but also that it is possible to adopt a multiple arrangement of different gas sensors sensitized to different components of the gas and, in correspondence therewith, to provide the appropriate number of different gas generators. There thus ensue, from the reduction in the structural size of the gas generators, not only constructional aspects but also functional ones, namely those for the detection of different components of the gas by means of the same device.

The development of gas by displacing the pH is of course basically known, but it is new when tied up in a manner in accordance with the invention. One obtains the wanted components of the gas by electrochemically acidifying or alkalisng a salt solution in combination with the corresponding acid/base reactions. The process of acidification or alkaisation is effected in the electrochemical manner described, by electrolysing water. The local changes in pH, which occur in the course of electrolysing aqueous solutions, are described in "pH-

Changes at Near-Electrode Surfaces, Journal of Applied Electrochemistry, 13 (1983) p 189".

In the present invention, the generation of the gas does  
 5 not occur by virtue of direct reactions at the electrodes but rather, by virtue of the secondary reactions of the actual products of the electrolysis.

When electrolysing aqueous solutions,  $H^+$  and  $OH^-$  ions are  
 10 formed in addition to the gases  $H_2$  and  $O_2$ . If these products of the reactions at the anodes and cathodes do not recombine, they can enter into further acid-base reactions. This situation is achieved in the present invention by virtue of the spatial separation of the  
 15 electrodes or, for obtaining a more compact structure, by means of divided cells which are separated either by means of diaphragms or ion exchange membranes. A further way of setting up this chemical situation is to fill the cells with inspissate or gel-like electrolyte so that  
 20 reduced ion migration speeds then occur. The following chemical reactions occur at the electrodes during the electrolysis of water

Equation 1: Cathode reaction:  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$   
 25 Equation 2: Anode reaction:  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

The increase in pH at the cathode occurs through the formation of the hydroxyl ion presented above in Equation  
 30 1. By contrast, a reduction in pH occurs at the anode due to the formation of protons (Equation 2). These displacements of the pH are localised to the vicinity of the respective electrodes when the electrolysis times are short. These displacements of the pH are again  
 35 neutralised, by diffusion and re-mixing when the cells are not divided. If, on the other hand, any intensive re-mixing of the electrolyte is avoided, for example, by

absorption in an appropriate absorption means, then the change in the pH values is locally very marked and acid/base reactions having high yields can be started.

5 Base gases can be produced by virtue of an increase in the pH and acidic gases can be produced by virtue of a decrease in the pH. For example, ammonia is developed by alkalyzing an aqueous solution of ammonium salts in accordance with the Equation 3 which is described  
10 hereinafter. If the cathode in the form of a sieve is located directly over the surface of the gas, then the ensuing ammonia can escape into the gas space together with the hydrogen which is likewise formed at the cathode. Equation 4 describes the production of CO<sub>2</sub> by  
15 acidifying a KHCO<sub>3</sub> aqueous solution for example.

The said reaction Equations 3 and 4 are as follows:

Equation 3:  $(\text{NH}_4)_2\text{SO}_4 + 2\text{OH}^- \rightarrow 2\text{NH}_3\uparrow + 2\text{H}_2\text{O} + \text{SO}_4^{2-}$   
20 Equation 4:  $\text{KHCO}_3 + \text{H}^+ \rightarrow \text{CO}_2\uparrow + \text{K}^+ + \text{H}_2\text{O}$

The invention is suitable for manufacturing all of the gases that can be produced by means of acid-base reactions insofar as these do not enter into any direct  
25 electrode reactions. The latter can be controlled however, by the selection of appropriate electro-catalysing materials.

The electrochemical cells may, as already mentioned  
30 above, be either divided or undivided. In a divided cell, the separation may be effected either by means of diaphragms or by means of corresponding ion exchange membranes. The undivided cell is realised, in the light of the chemical situation mentioned above, by virtue of  
35 distancing the electrodes sufficiently, by using inspissate electrolytes or by use of gel electrolytes.

Thus, overall, by making use of the method in accordance with the invention in the equipment in accordance with the invention, one obtains the result that the generator as such, has an extremely small structure. Consequently, it is possible to integrate them into likewise small-sized gas monitoring or gas analysing devices. From this, there results a usage in accordance with the invention, in portable gas warning devices. Moreover, due to the miniaturisability of the equipment, which also results from the method of operation, there likewise arises the possibility of integrating a whole series of gas generators for different components of the gas into a device which is correspondingly equipped with different sensors and which can thus detect different gases.

#### BRIEF SUMMARY OF THE DRAWINGS

The invention is illustrated in the drawing and will be explained in more detail hereinafter.

Figure 1 shows a schematic sketch of the equipment in accordance with the invention and

Figure 1 shows, in the left part, a gas generator cell using a gel electrolyte and, in the right part, a gas generator cell using an aqueous solution as the electrolyte.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

Figure 1 shows a system which can be utilised, for example, in gas warning devices or gas analysing devices. A gas sensor 1 is disposed within a housing 10. The housing 10 is open at the location 3 and the gases to be analysed can thus enter. Furthermore, the gas sensor 1 is provided with an entrance opening 5 through which the gas that is to be tested can enter into the sensor. For the



that is to be tested can enter into the sensor. For the case that the sensor 1 is sensitized to an extremely poisonous gas i.e. in the event that correspondingly toxic gases have to be released by the generator cell 2, the opening 3 can be closed by the cover 11 during the test phase. A fan 4 is provided in order to supply the gas released by the generator cell 2 to the sensor 1. It is important to mention here, that only temporary quantities of gas are released by the generator i.e. amounts of gas are released for only short periods of time. This is realised by means of an electrical control means which is not further illustrated here.

In the upper part of the picture, Figure 2 shows a system for producing  $\text{NH}_3$  which can be utilised as a generator cell 2 in an arrangement in accordance with Figure 1. A gel 100 comprising ammonium sulphate is located between two platinum electrodes 20 and 30 of which the upper electrode 20 is implemented in the form of a grid. The upper electrode is connected up as a cathode 20, the lower one as an anode 30. When implementing the water electrolysis, ammonia and hydrogen, which diffuse away from the generator cell, escape from the cathode 20 into the gas space 40. After the current has been switched off, the concentration profiles for the individual ions rebalance themselves by means of a diffusion process in the gel, and the cell is then ready again to produce fresh surges of gas by means of which the monitoring of the gas sensor is effected. If a gel type electrolyte is not used but rather, an aqueous solution of ammonium sulphate is used as the electrolyte, then, as described above, the chemical situation illustrated is set up by dividing up the generator cell. This situation is illustrated in the lower part of Figure 2. Here, the generator cell is divided by an ion exchange membrane 60 which, for example, may consist of "Nafion" from the

DuPont Company. The lower surface of the sensor leads into the counter electrode gas space 50.

Defined surges of gas can be produced for example, by  
5 operating the current source in pulsed manner, the surges  
being adapted, as regards their strength or intensity and  
duration, to the sensitivity of the test cell that is to  
be monitored. Pulsed operation has the additional  
advantage that the electrolysis can be implemented at  
10 middling to high current densities, whence high product  
yields thereby occur. When integrating such a gas  
generator into a gas warning device, it is not only  
important for the realisation of the invention that the  
gas generator should also release the gas component, to  
15 which the sensor is sensitized, in sufficient quantities,  
but also that the quantity released must be matched in  
appropriate manner to the detection limits and to the  
test range of the sensor. Furthermore, as already  
presented above, one must take care, in the case of  
20 highly toxic gases, that gas-dynamics and/or device-  
related safety measures should be built in, the measures  
being such as to avoid external exposure to poisonous  
gases when portable gas warning devices that are to be  
worn by personnel are put into use. However, for the case  
25 where the devices, although they are portable, are  
usually employed for operation in working areas in which  
personnel are present, for example, by being hung on a  
wall, then, in dependence on the selection of the test  
gas, such safety precautions are not necessary.

30

## CLAIMS

1. Method of monitoring gas sensors in which temporary quantities of gas of the test component are produced and  
5 are supplied to the gas sensor for monitoring the sensitivity and/or the response time and/or the regenerative behaviour thereof, the improvement consisting in that, one proceeds in such a way that local pH displacements  
10 occur due to acidification at the anode and alkalinity at the cathode by virtue of a water electrolysis process and the quantities of gas required for monitoring the sensor are produced at the anode and/or at the cathode.
- 15 2. Method of monitoring gas sensors as in Claim 1, wherein, the quantity of gas required for monitoring is transposed into a stream of gas and the sensor is subjected to the gas stream of the test gas component that has been  
20 produced.
3. Method of monitoring gas sensors as in Claim 1, wherein, the place where the gas quantities required for the  
25 monitoring are produced is a gas space in which the gas sensor is also disposed.
4. Equipment for monitoring a gas sensor including a gas generating cell which can be connected to the gas sensor  
30 in a manner which ensures the flow of gas therebetween and which temporarily releases quantities of test gas when it is temporarily subjected to an electrical current, the improvement consisting in that,  
35 the gas sensor and the gas generating cell lead, insofar as their gas absorbing or gas desorbing surfaces are concerned, into a common gas space and that there are

provided electrically and/or mechanically actuatable means which prevent any escape of the quantities of test gas from the gas space during the test phase.

- 5    5. Equipment for monitoring a gas sensor as in Claim 4, wherein,  
the gas generating cell is an electrolytic cell.

6. Equipment for monitoring a gas sensor as in Claim 4, wherein, the electrically and/or mechanically actuatable means consists of an electrically closable cover.

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7. Equipment for monitoring a gas sensor as in Claim 4, wherein, the electrically and/or mechanically actuatable means comprises an element for producing gas streams, which element concentrates the quantities of test gas on the gas sensor during the test phase.

10

8. Portable gas warning device including a gas generator functioning as in the method Claim 1.

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9. Portable gas warning device including a gas generator as in the apparatus Claim 4.

20

10. Portable gas warning device including at least one gas generator functioning as in the method Claim 1.

25

11. Portable gas warning device including a plurality of sensors which are sensitized to different components of the gas and including a plurality of gas generators that produce the different components of the gas.

12. Methods of monitoring gas sensors as claimed in claim 1 and as herein described.

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13. Equipment for monitoring gas sensors as claimed in claim 4 and as herein described.

14. Portable gas warning devices as claimed in claim 11 and as herein described.

35



Application No: GB 9514055.4  
Claims searched: 1 - 3, 8, 10 and 12.

Examiner: D J Mobbs  
Date of search: 4 October 1995

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.N): C7B BCAX; G1B BBS; G1N NAHK, NAHAS, NBKT, NCGB.  
Int CI (Ed.6): G01N 33/00.  
Other: ONLINE: WPI, CLAIMS, JAPIO.

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 2254696 A THORN EMI	1, 3, 8, 10
X	GB 1552538 BAYER - see particularly page 7 line 43 - page 8 line 53. (equivalent to DE 2621677)	1, 2
Y	US 4460448 DOW CHEMICAL	1, 2
Y	Chemistry in Britain, February 1975, pages 59 - 64, Indirect Electrochemical Processes, Clarke et al.	1 - 3, 8, 10

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.